Development of an Automated Phase Behaviour Determination of Lean Hydrocarbon Fluid Mixtures with Re-Entrant RF/Microwave Resonant Cavities[1]

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[1] Paper presented at the Fourteenth Symposium on Thermophysical Properties, June 25-30, 2000, Boulder, Colorado, U.S.A.

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ABSTRACT

A re-entrant resonator has been developed and tested, specifically tailored for automated phase boundary measurements in the natural gas fluids of the North West Shelf of Western Australia. The resonator is based on a constant volume, RF re-entrant resonant cavity capable of detecting phase boundaries in binary mixtures [1]. Our resonator is capable of isothermal and isobaric measurements in addition to isochoric measurements.

The vacuum characteristics of the resonator have been studied using extensive models, and measured in experiments with helium. The resonator was then employed to study phase transitions in pure carbon dioxide and a binary mixture of propane and carbon dioxide. The suitability of the resonator for dew point detection in lean hydrocarbon mixtures was also tested. The results indicate that microwave resonators are not just limited to phase boundary measurements: rather they can measure phase volumes and potentially determine the compositions of the two phases. However, further development is needed to achieve a system in which accurate measurements can be made for gas condensate type fluids.

KEY WORDS: dew point; dielectric constant; fluid mixtures; microwave resonant cavity; natural gas; phase behaviour.

1. INTRODUCTION

An understanding of the phase behaviour of hydrocarbon mixtures is essential to all areas of the petroleum industry. The fluid's dew point curve is particularly relevant to the production of lean hydrocarbon mixtures, such as the natural gas and gas condensate fluids found on the North West Shelf of Western Australia. Dew points are highly sensitive to the vanishingly small fractions of higher alkanes in the fluid, and prediction of the dew point curve with thermodynamic models is notoriously unreliable. Given the economic value of phase behaviour information, experimental measurement is the only sufficiently accurate means of determining the dew point curve.

When in the two-phase state, at most temperatures and pressures of interest, the lean nature of these fluids results in a relatively small liquid volume fraction. Measurement of the slope discontinuity in the dielectric properties of a fluid at a phase change has been at the heart of phase behaviour measurement systems based on RF and microwave cavities in existence since 1985 [2]. Microwave systems have the potential to be vastly superior to expensive conventional volumetric systems, mainly due to their small sample volumes. In 1996, the development of a constant volume re-entrant resonator [1], complete with an accurate waveguide model, significantly advanced the development of microwave detection of phase boundaries. The re-entrant resonator was used successfully to detect dew and bubble points in the vicinity of the critical point of a binary mixture of carbon dioxide and ethane.

Constant volume systems are not adequate for measurements in naturally occurring hydrocarbon mixtures, as varying the density by injecting additional sample can often

lead to inadvertent changes in composition. Density variation while maintaining constant composition is essential to achieve a complete and accurate phase envelope. We report here the development of a *variable volume* resonator, which has the capability of performing isothermal and isobaric as well as isochoric measurements, and it has been tested on both pure fluids and mixtures to guide further experimental development.

2. THE VARIABLE VOLUME MICROWAVE RESONATOR

2.1 Description

The variable volume resonator, shown in figure 1, consists of a stainless steel pressure cylinder terminated at one end by a brass re-entrant cavity and at the other by a floating piston. The cavity is similar to Moldover's cavity [1] but, because fluid is present on both sides of the cavity's (cylindrical) walls, there is no dilation of the principal capacitance gap when the cavity is subject to pressure. Furthermore, the hole in the base of the cavity is dimensioned to ensure high attenuation of r.f. fields without impeding fluid flow. The cavity's resonant frequency is therefore completely insensitive to the position of the piston, which floats on a hydraulic fluid. The volumetric compression, inferred from the volume of hydraulic fluid injected, is approximately 10:1 and the entire system can be operated at pressures up to 150 bar.

2.2 Modelling

Moldover *et al.* developed an analytical waveguide model of their resonator relating the resonant frequency to the cavity's dimensions, based on standard coaxial waveguide theory. The model also incorporated fringing field estimates [3], which ultimately

placed a limit on the model's accuracy (~ ± 5 MHz). We have used Finite Element Analysis [FEA] to solve the electromagnetic field equations to the required precision. In addition we have used FEA to solve the elastic equations in order to quantify the small residual deformation of the cavity under pressure. The FEA deformation predictions for both Moldover's cavity and our resonator were input into electromagnetic FEA models to predict the effect of deformation on vacuum frequency.

2.3 Experimental System

To determine and track the resonant frequency of the cavity, a Pound frequency discriminator circuit is used [4]. The resonator is excited by a carrier from a function generator (HP8647A), which is also frequency modulated at 80 kHz. The signal is transmitted through or reflected from probes attached to SMA glass-to-metal feedthroughs soldered into the cavity lid. The frequency offset between the carrier and the resonator appears as 80 kHz amplitude modulation, which is demodulated by a diode and a lock-in amplifier. The latter is used in a feedback loop to track the resonator's centre frequency.

Figure 1 also contains a schematic of our system. A thermistor, calibrated over the temperature range 30°C to 120°C against a standard platinum resistance thermometer, and accurate to 20 mK, is mounted in the thin neck of the cavity. A resistive heater and fan-forced oven are incorporated in a PID control loop, which maintains the resonator's temperature to within the accuracy bounds of our thermistor. A Quartzdyne Series QS High Pressure Transducer, with an accuracy of 0.01%, is used to measure the pressure. It was calibrated against a Desgrange et Huot primary pressure standard. An ISCO

μLC-500 micro flow syringe pump is used to pump hydraulic fluid to the underside of the floating piston. A circulating pump similar to that used by Moldover *et al*. is used to remix samples that have undergone separation into two phases of differing composition. The pump achieves speeds of the order of 1 cm^3/s and is capable of generating a pressure head of 2.5 kPa, extracting fluid from the top of the brass cavity, and returning it to the pressure cylinder. A desktop PC with a GPIB card and LabView software is used for data acquisition, frequency tracking and thermal control, and also to provide real-time plots of the resonator's frequency, temperature and pressure. In systems in which the phase transition signal is large these plots allowed real-time observation of the transition.

3 EXPERIMENTAL RESULTS

3.1 Vacuum and Helium Results

The vacuum resonant frequency was measured to be about 645 MHz, compared to the waveguide and finite element resonant frequency predictions of 631 MHz and 637.3 MHz respectively. The majority of the discrepancy between these values is attributed to uncertanties in the re-entrant cavity's dimensions. The temperature coefficient of the evacuated resonator, $\partial(\ln f_o)/\partial T$, was measured to be $(-20.12 \pm 0.02)\times10^{-6}\,K^{-1}$, in excellent agreement with literature values of brass' thermal expansion coefficient [5].

The effect of dimensional changes, due to pressure, on the empty cavity were deduced by performing an isothermal experiment at 313.00 K with 99.9% pure helium as the cell fluid. The pressure of the helium was increased in 5 bar increments up to 50 bar, and the resonant frequency tracked. At each pressure the dielectric constant of helium was

calculated accurately from a virial expansion of the Clausius-Mosotti [CM] relation [1], which was then used to calculate the vacuum frequency. This allowed us to determine the resonator's frequency pressure dependence, $\partial(\ln f_0)/\partial p$, to be $(-2.2 \pm 0.2)\times10^{-6}$ bar^{-1}, an order of magnitude smaller than Moldover's value, and with the opposite sign. Our combined elastic–electromagnetic FEA model correctly predicted the sign of the effect and was in reasonable agreement with its magnitude. The FEA model also correctly predicted Moldover's experimentally determined value of $\partial(\ln f_0)/\partial p = 2.9\times10^{-5}$ bar^{-1}.

3.2 Carbon Dioxide Results

Approximately 0.45 moles of industrial grade (99.9%) carbon dioxide was admitted to the resonator at maximum volume (185 mL) and 295.00 K. The resonant frequency was then tracked while the piston continuously and isothermally compressed the CO_2. Being a single component fluid, there was no requirement for mixing, allowing the measurement to be performed relatively quickly via a continuous pressure scan. The limiting compression rate was determined by the sample's thermal equilibration time and the response time of the Pound system.

Figure 2 shows both the resonant frequency and pressure as a function of mass density across the isotherm. Bender's equation of state [6] was used to estimate the fluid's initial density. The agreement between the measured and predicted pressure isotherms was good bearing in mind that the system is only in dynamic equilibrium. The deviation of the experimental pressure from the saturation pressure in the vicinity of the bubble point is attributed to liquid CO_2 being forced through capillary tubing external to the cavity. The frequency "signature" of the CO_2 fluid as it was compressed across the two-

phase region confirms that microwave systems can measure phase volumes in addition to phase boundaries. The changes in its slope at points D and B correspond to the dew and bubble points of the isotherm. The slope changes in the frequency curve at points A and C are of more significance, since in a pure fluid the phase change can be readily identified from the slope of the pressure versus density curve. These slope changes identify the location of the liquid phase within the cavity as they correspond to changes in the capacitance region that is being filled with liquid. The section of the curve with the greatest slope corresponds to the liquid filling the 1 mm-annular gap that comprises the principal capacitance of the cavity.

3.3 Binary Mixture Results: (0.495 C_3H_8 + 0.505 CO_2)

Figure 3 shows the frequency signature of a close boiling binary mixture consisting of 49.5% C_3H_8 and 50.5% CO_2, which was first isothermally compressed, and then isothermally expanded, at 310.00 K, across the two-phase region. (The mixture was prepared and analysed by Alinta Gas Research Laboratories using research grade gases.) Volume measurements were converted to densities using the Peng-Robinson equation of state [PREOS]. In addition to the slope changes corresponding to the dew and bubble points, the dramatic slope changes as liquid fills the cavity provide a measure of the phase volumes. The hysteresis exhibited as the direction along the isotherm is reversed occurred because the mixing pump was not employed during the scan, and once the fluid entered the two-phase region a compositional stratification resulted. This stratification also made detection of the phase boundaries “directionally dependent”: the dew point was easiest to detect as density was increased (no prior stratification), whereas the bubble point was easiest to detect as density was decreased.

To verify this stratification, at the conclusion of the experiment, samples were taken from the resonator and analysed by a gas chromatograph. The fraction of C_3H_8 was 0.50, 0.56 and 0.66 at the "top", "middle" and "bottom" of the resonator respectively. Although the sampling method was somewhat crude, the results indicate that the liquid phase, richest in C_3H_8, fell to the bottom of the resonator while the fluid was in the two-phase region.

Figure 4 shows a measurement of the 310.00 K isotherm's dew point made by increasing the pressure in discrete 0.5 bar intervals across the phase boundary. The system was allowed to come to equilibrium at each point, indicated by the stability of the frequency to within preset limits. Equilibrium was achieved by using the re-circulation pump for half an hour, then allowing the fluid to settle for a further half-hour. The frequency and pressure were then averaged over a final half-hour period. The PREOS predicted the dew point to be at 28.25 bar, whereas the resonator allowed us to observe the formation of liquid in real-time at about 28.0 bar. Figure 5(b) shows this real-time plot. Generally, increasing pressure corresponds to decreasing resonant frequency as an increase in the fluid's density corresponds to an increase in its dielectric constant, as illustrated in figure 5(a). The only way the frequency can increase with pressure is if the vapour phase's dielectric constant decreases as a liquid phase is formed, as in figure 5(b).

Non-linear least squares regression of the entire data set (figure 4) to a four parameter (dew point coordinates, single phase and two-phase slopes) function gave a measure of the dew point at (310.00 ± 0.02 K, 27.78 ± 0.07 bar). The error bound on the dew point

pressure is the standard 1σ confidence level whereas the temperature error bound is the thermistor's accuracy. Samples were again taken from the "top", "middle" and "bottom" of the resonator and analysed on a gas chromatograph. In this case no significant discrepancies existed between the compositions measured at each level, indicating that the re-circulation pump had proved effective.

Isochoric measurements in fluid mixtures produce optimum microwave signals. In the single-phase region the fluid's constant density results in a constant resonant frequency (zero slope), whereas in the two-phase region the phase densities vary, resulting in a non-zero frequency slope. The two intersecting lines are distinct and the phase transition is readily identified Isothermal or isobaric measurements cannot take full advantage of this density discontinuity and typically produce slopes that are less distinct. The difference between measurement pathways is most acute when investigating fluids, such as close boiling binary mixtures, that have a relatively small two-phase area in the P-T plane. A small two-phase region indicates that rapid changes in each phase's volume and composition occur for relatively small changes in pressure and temperature. However, lean hydrocarbon mixtures have large two-phase areas and consequently the vapour phase density discontinuity at the dew point is negligible. Thus, while close boiling binary mixtures produce large microwave signals, which are further optimised by isochoric measurements, in microwave systems that principally interrogate the vapour phase, there is little difference between measurement pathways in lean hydrocarbon mixtures.

3.4 Lean Natural Gas Mixture Measurements

The phase envelope of a hydrocarbon sample from a North West Shelf process stream was measured in our laboratory along several isotherms. This measurement program employed a gas condensate volumetric PVT cell, optimised for lean gas dew point measurements. The fluid was extremely lean: the C_4+ fraction comprising less than 2% of the sample by mole fraction. Such a fluid mixture represents the ultimate test for any system attempting to measure or predict its dew point curve. The PVT cell data on the 293.6 K isotherm gave both the upper and lower dew points and each differed from the equation of state predictions by more than 25 bar. In a total sample volume of over 2000 cm^3, the maximum liquid volume measured by the PVT cell on this isotherm was 0.3 cm^3. A compositional flash calculation at this maximum liquid volume condition indicated that no component in the vapour phase had a mole fraction that differed from the overall composition by more than a few parts in 10^4. This was therefore an ideal fluid mixture to test the microwave technique.

The CM-relation, assuming a mole-fraction average of this function for mixtures, was combined with the flash results to estimate the change in the vapour phase's dielectric constant due to the formation of 0.3 cm^3 of liquid in a 2000 cm^3 gas sample. The calculation indicated a +30 kHz shift from the single-phase frequency (~ 600 MHz). compared to a –5100 kHz shift resulting from the decrease in pressure. This background "noise", due primarily to the expansion of methane, effectively set the microwave signal to noise ratio at this maximum liquid volume to 6×10^{-3}.

Thus, such a mixture may be expected to represent the "lean boundary" of fluid mixtures in which microwave systems based on Moldover's re-entrant geometry can detect dew point signals. This was tested and confirmed experimentally; scans of this mixture along the 293.60 K isotherm did not give reproducible liquid phase signals. A more sensitive system for lean fluids, capable of clear determination of dew points and liquid volumes, is under development.

4 CONCLUSION

The work of Moldover *et al.* has provided the inspiration for the development of a phase behaviour measurement system based on a re-entrant microwave resonant cavity, specifically tailored for lean hydrocarbon fluid mixtures. The most important modification was the incorporation of a variable volume capability into the resonator.

The resulting prototype instrument has been well modelled, has demonstrated a capability of detecting dew and bubble points in pure fluids and binary mixtures and has shown that microwave systems have the capability of measuring phase volumes. The research has revealed that a re-circulation system is essential for accurate measurements in fluids and that isochoric measurements give the largest signals. We have explored the compositional sensitivity of resonators similar to Moldover's and their limitations in mapping out a dew point curve in ultra lean fluids.

Current work is under way to optimise the resonator's geometry in order to improve measurements not only of phase envelopes, but also quality lines and compositions in very lean gas condensate fluids.

5 LIST OF SYMBOLS

f_0 Cavity's resonant frequency

p Pressure

T Temperature

6 ACKNOWLEDGMENTS

This work was supported by the Australian Research Council. We would like to thank Graeme Warburton, Chris Ballam and John Budge for the construction of the resonator and associated system. We would also like to thank Rob Trengove, Courtney Milner, and Leah Ronan for their support of the project and acknowledge the work of Chris Hines and Shane McCarthy who initiated the finite element modelling. Finally, we would like to thank David Manning at Vision Reservoir Management Technologies International and Woodside Energy Ltd. for their support of this project.

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Figure 1. Cross-section of the variable volume resonator and schematic of experimental system: 1. Indium O-Ring, 2. SMA Feedthrough, 3. Inlet Valve, 4. Circulation Pump, 5. Thermistor, 6. Brass Cavity, 7. SS Pressure Cylinder, 8. Hydraulic Piston, 9. Resistive Heater, 10. Hydraulic Pump, 11. Fan-forced oven

Figure 2. CO_2 Results: Measured Frequency (blue) and Pressure (black) as a function of Density along 295 K isotherm.

Figure 3. Scan up and down along 310 K isotherm in $0.495C_3H_8$+$0.505CO_2$ mixture.

Figure 4. Dew Point Measurement along 310 K isotherm in $0.495C_3H_8$+$0.505CO_2$ mixture.

Figure 5. Real-time plots of 27.5 bar (point 1 in figure 4) and 28 bar (point 2 in figure 4) data points along 310 K isotherm in $0.495C_3H_8$+$0.505CO_2$ mixture. Frequency (pink squares) and pressure (blue triangles) vs time.

Figure 1.

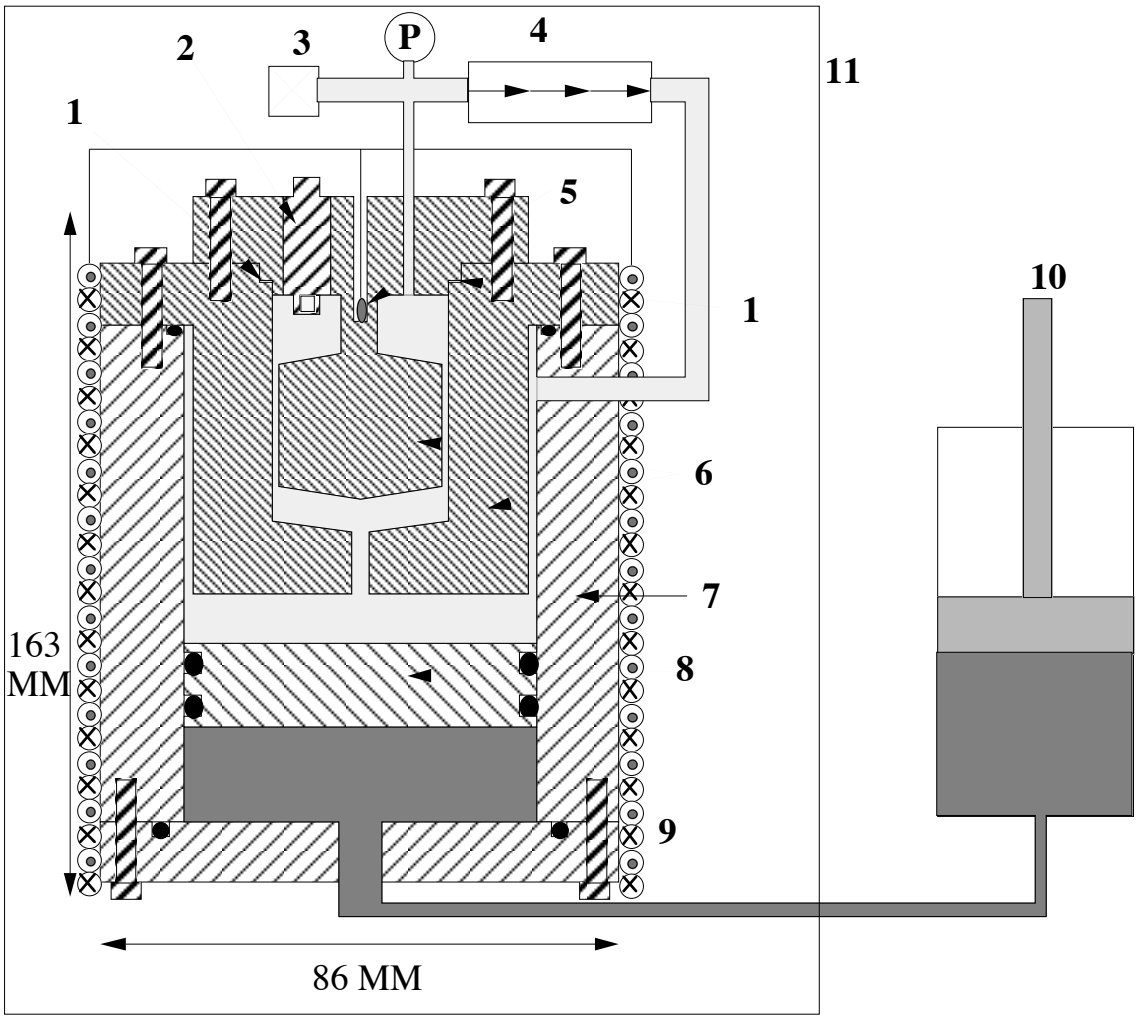

Figure 2.

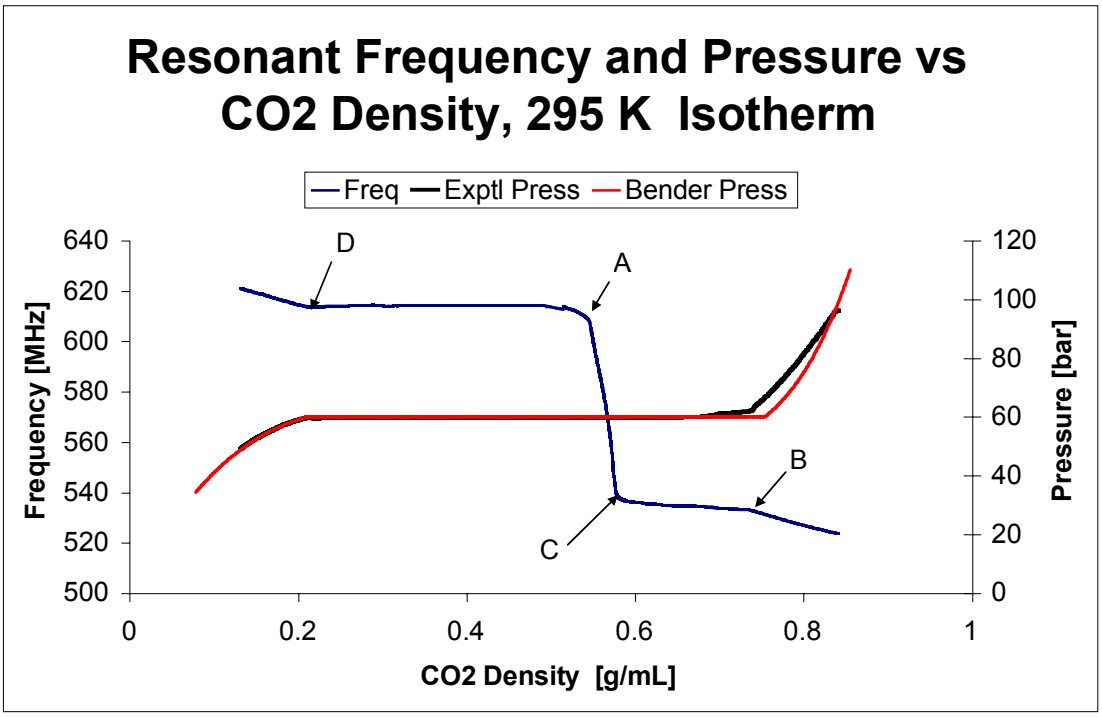
Resonant Frequency and Pressure vs CO2 Density, 295 K Isotherm
Freq
Exptl Press
Bender Press
Frequency [MHz]
640
620
600
580
560
540
520
500
Pressure [bar]
120
100
80
60
40
20
0
0
0.2
0.4
0.6
0.8
1
CO2 Density [g/mL]
A
B
C
D

Figure 3

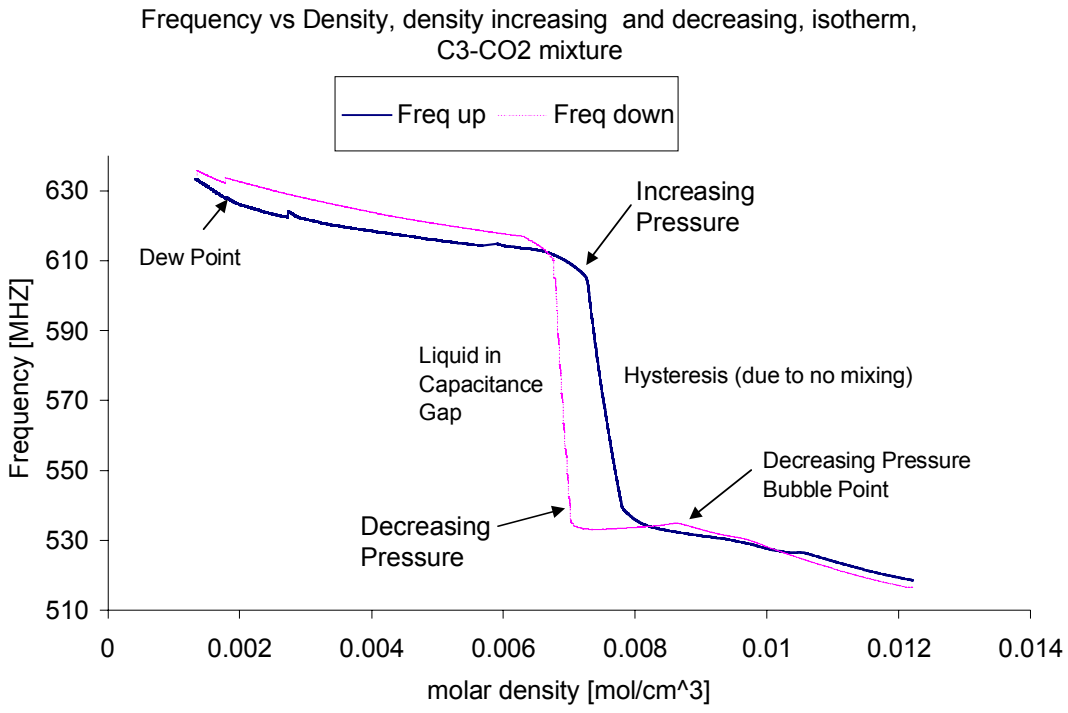
Frequency vs Density, density increasing and decreasing, isotherm, C3-CO2 mixture
Freq up
Freq down
Frequency [MHZ]
630
610
590
570
550
530
510
0
0.002
0.004
0.006
0.008
0.01
0.012
0.014
molar density [mol/cm^3]
Dew Point
Increasing Pressure
Liquid in Capacitance Gap
Hysteresis (due to no mixing)
Decreasing Pressure Bubble Point
Decreasing Pressure

Figure 4

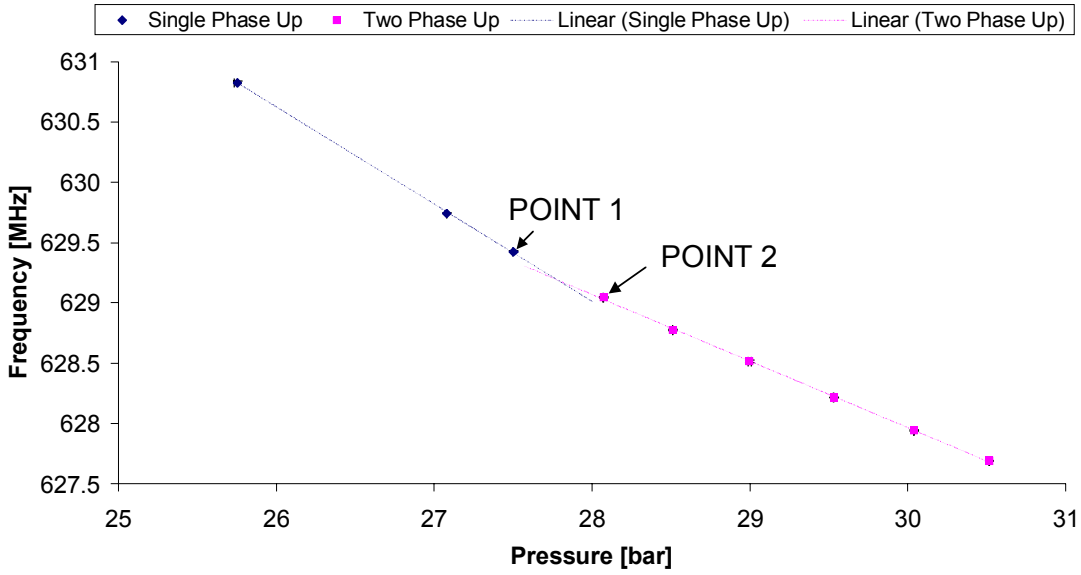
Single Phase Up
Two Phase Up
Linear (Single Phase Up)
Linear (Two Phase Up)
631
630.5
630
629.5
629
628.5
628
627.5
Frequency [MHz]
25
26
27
28
29
30
31
Pressure [bar]
POINT 1
POINT 2

Figure 5

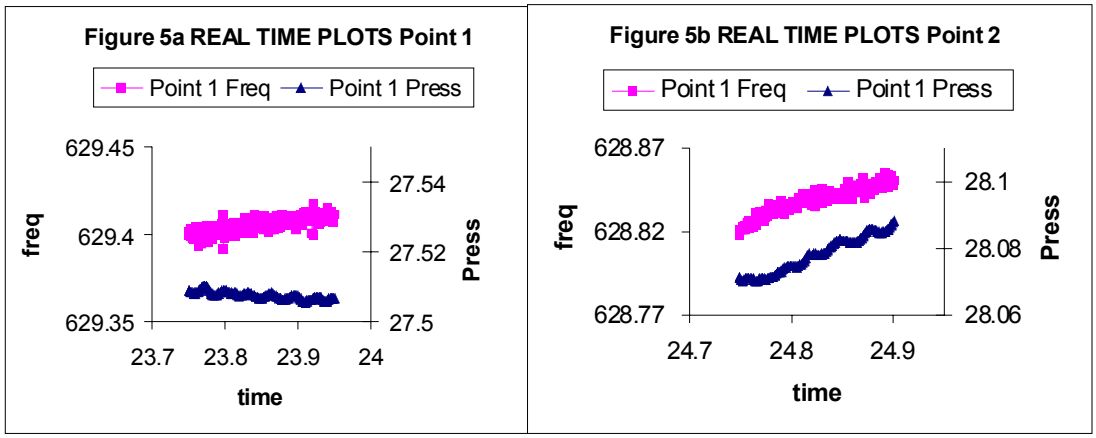
Figure 5a REAL TIME PLOTS Point 1
Point 1 Freq
Point 1 Press
629.45
629.4
629.35
freq
27.54
27.52
27.5
Press
23.7
23.8
23.9
24
time
Figure 5b REAL TIME PLOTS Point 2
Point 1 Freq
Point 1 Press
628.87
628.82
628.77
freq
28.1
28.08
28.06
Press
24.7
24.8
24.9
time